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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS/REPORTS

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**NEW THERMAL CURING COMPOSITE MATRICES,  
RIGID ROD POLYMERS, AND SOLID-STATE NMR**

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1 June 1990



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## Part I

### A. Papers Submitted to Refereed Journals

"Addition Polymerization of 1-Cyclobutenecarboxylic Acid: A Novel Polyacrylic Acid Analog," L.J. Mathias and P.K. Casey, submitted to Polymer.

"A Spectra Calc-based NMR Module for Processing Bruker NMR Files on a PC", P.K. Casey, W.L. Jarrett and L.J. Mathias, submitted to **Scientific Computing**.

"Natural Abundance  $^{15}\text{N}$  CP/MAS NMR of Solid Polyamides: A Technique Sensitive to Crystalline Composition and Conformation," D.G. Powell, A.M. Sikes and L.J. Mathias, revised and resubmitted to **Polymers**. (Technical Report #24).

"Solid State  $^{15}\text{N}$  NMR of  $^{15}\text{N}$ -labeled Nylon 6 and Nylon 11," L.J. Mathias, D.G. Powell, J.-P. Autran and R.S. Porter, **Mat. Sci. Engn.**, in press. (Technical Report #33).

### B. Papers Published in Refereed Journals

" $^{15}\text{N}$  T<sub>1</sub> Measurements of Semicrystalline Nylon 6," D. G. Powell and L. J. Mathias, **Macromolecules**, 1989, **22**, 3812-3814. (Technical Report #22).

" $^{15}\text{N}$  NMR Powder Spectra of Semicrystalline Nylon 6," D. G. Powell and L. J. Mathias, **Polym. Comm.**, 1990, **31**, 58-60. (Technical Report #23).

"Characterization of Nylon 6 by  $^{15}\text{N}$  Solid State Nuclear Magnetic Resonance," D. G. Powell and L. J. Mathias, **J. Am. Chem. Soc.**, 1990, **112**, 669-675. (Technical Report #25).

" $^{15}\text{N}$  NMR Characterization of Multiple Crystal Forms and Phase Transition in Polyundecanamides," L. J. Mathias, D. G. Powell, J. -P Autran and R. S. Porter, **Macromolecules**, 1990, **23**, 963-967. (Technical Report #26).

### C. Books (and sections thereof) Submitted for Publication

none

### D. Books (and sections thereof) Published

Mathias, Lon J., Colletti, Ronald F., Halley, Robert J., Jarrett, William L., Johnson, C. Greg, Powell, Douglas G., and Warren, Stephen C., Solid-State NMR Polymer Spectra Collected Volume I, MRG Polymer Press, Hattiesburg, MS 1990.



Availability Codes	
Dist	Avail and/or Special
A-1	

**E. Technical Reports Published (including ONR Technical Reports) and Papers Published in Non-Refereed Journals**

Technical Report #26: "<sup>15</sup>N NMR CHARACTERIZATION OF MULTIPLE CRYSTAL FORMS AND PHASE TRANSITION IN POLYUNDECANAMIDES," by *Lon J. Mathias, Douglas G. Powell, Jean-Philippe Autran and Roger S. Porter*

Technical Report #27: "<sup>15</sup>N NMR CHARACTERIZATION OF MULTIPLE CRYSTAL FORMS AND PHASE TRANSITIONS IN POLYUNDECANAMIDE (NYLON 11)" by *Lon J. Mathias, Douglas G. Powell, Jean-Philippe Autran and Roger S. Porter*

Technical Report #28: "NMR STUDY OF ARAMID MODEL COMPOUNDS" by *Lon J. Mathias, Masaru Yoneyama and William L. Jarrett*

Technical Report #29: "GENERAL DATA PROCESSING STATION FOR MODERN SPECTROMETERS" by *Lon J. Mathias, Paul K. Casey and William L. Jarrett*

Technical Report #30: "SOLID-STATE <sup>13</sup>C NMR STUDY OF POLYETHYLENE REACTOR POWDERS" by *Lon J. Mathias, William L. Jarrett and Roger S. Porter*

Technical Report #31: "RADICAL HOMOPOLYMERIZATION OF A TRISUBSTITUTED ALKENE: 1-CYCLOBUTENECARBOXYLIC ACID" by *Lon J. Mathias and Paul K. Casey*

Technical Report #32: "SOLID-STATE NMR CHARACTERIZATION OF  $\alpha$ -NYLON 12" by *Lon J. Mathias and C. Greg Johnson*

Technical Report #33: "SOLID-STATE <sup>15</sup>N NMR OF <sup>15</sup>N-LABELED NYLON 6 AND NYLON 11," by *Lon J. Mathias, Douglas G. Powell, Jean-Philippe Autran and Roger S. Porter*

**F. Patents Filed**

none

**G. Patents Granted**

none

**H. Invited Presentations at Topical or Scientific/Technical Society Conferences**

"Solid State <sup>15</sup>N NMR of Nylons"

L.J. Mathias

Chemistry Department, University of Arkansas at Little Rock, AR, April 2, 1990.

**" $^{15}\text{N}$  NMR Characterization of Multiple Crystal Forms and Phase Transitions in Polyundecanamide (Nylon 11)"**

Lon J. Mathias, Douglas G. Powell, Jean-Philippe Autran and Roger S. Porter

199<sup>th</sup> American Chemical Society National Meeting, Boston, MA, April 22-27, 1990.

(Technical Report #27)

**I. Contributed Presentations at Topical or Scientific/Technical Society Conferences**

**"Solid-State  $^{15}\text{N}$  NMR of  $^{15}\text{N}$ -Labeled Nylon-6"**

Lon J. Mathias and Douglas G. Powell

45<sup>th</sup> ACS Southwest Regional Meeting, Baton Rouge, LA, December 6, 1989.

**"Molecular Dynamics of Polymers Using Size-State Deuterium NMR"**

Ronald F. Colletti and Lon J. Mathias

45<sup>th</sup> ACS Southwest Regional Meeting, Baton Rouge, LA, December 6, 1989.

**"Use of Labeled Materials for the NMR Characterization of Aramids"**

Lon J. Mathias, Masaru Yoneyama and William L. Jarrett

45<sup>th</sup> ACS Southwest Regional Meeting, Baton Rouge, LA, December 6, 1989.

**"Synthesis and  $^{15}\text{N}$  CP/MAS NMR Analysis of  $^{15}\text{N}$ -Labeled Nylon 12"**

Lon J. Mathias and C. Greg Johnson

45<sup>th</sup> ACS Southwest Regional Meeting, Baton Rouge, LA, December 6, 1989.

**"Solid State  $^{15}\text{N}$  NMR of Nylons"**

Lon J. Mathias, Douglas G. Powell and Allison M. Sikes

The 1989 International Chemical Congress of Pacific Basin Societies, Symposium on Advances in Polymer Characterization, Honolulu, HI, December 20, 1989.

**"Solid-State Deuterium NMR of Nylon 6 and 11"**

Lon J. Mathias and Ronald F. Colletti

199<sup>th</sup> American Chemical Society National Meeting, Boston, MA, April 22-27, 1990.

**"Synthesis and Solid State NMR of  $^{15}\text{N}$ -Labeled Nylon 12"**

Lon J. Mathias and C. Greg Johnson

199<sup>th</sup> American Chemical Society National Meeting, Boston, MA, April 22-27, 1990.

**"NMR Study of Aramid Model Compounds"**

Lon J. Mathias, Masaru Yoneyama and William L. Jarrett

199<sup>th</sup> American Chemical Society National Meeting, Boston, MA, April 22-27, 1990.

**"General Data Processing Station for Modern Spectrometers"**

Lon J. Mathias, Paul K. Casey and William L. Jarrett

199<sup>th</sup> American Chemical Society National Meeting, Boston, MA, April 22-27, 1990.

**"Solid-State  $^{13}\text{C}$  NMR Study of Polyethylene Reactor Powders"**

Lon J. Mathias, William L. Jarrett and Roger S. Porter

200<sup>th</sup> American Chemical Society National Meeting, Washington, DC, August 26-31, 1990.

**"Radical Homopolymerization of a Trisubstituted Alkene: 1-Cyclobutenecarboxylic Acid"**

Lon J. Mathias and Paul K. Casey

200<sup>th</sup> American Chemical Society National Meeting, Washington, DC, August 26-31, 1990.

**"Solid-State NMR Characterization of  $\alpha$ -Nylon 12"**

Lon J. Mathias and C. Greg Johnson

200<sup>th</sup> American Chemical Society National Meeting, Washington, DC, August 26-31, 1990.

**"Solid State  $^{15}\text{N}$  NMR of Nylons: A Useful Method for Analysis of Crystal Forms and Molecular Motion"**

Lon J. Mathias, Douglas G. Powell, Jean-Philippe Autran and Roger S. Porter

IUPAC International Symposium on Specialty Polymers, Singapore, Republic of Singapore, November 7-9, 1990.

**J. Honors/Awards/Prizes**

none

**K. Number of Graduate Students Receiving Full or Partial Support on ONR Grant or Contract**

**TOTAL:**

Two (full-time): R.F. Colletti, P.K. Casey

One (part-time/graduated): D.G. Powell

Two (part-time, starting 7-1-90): R. Johnson, R. Sundar

**MINORITIES:** none

**ASIAN:** none

**L. Number of Postdoctoral Fellows Receiving Full or Partial Support on ONR Grant or Contract**

**TOTAL:**

One (full-time): W.L. Jarrett

**MINORITIES:** none

**ASIAN:** none

**M. Other Funding**

<b>Agency</b>	<b>Grant Title</b>	<b>Amount</b>	<b>Period of Performance</b>
National Science Foundation	Captodative Monomers and Polymers	\$65,000	11/30/89 - 12/1/90
Petroleum Research Fund	Captodative Monomers and Initiators	\$20,000	9/1/89 - 8/31/90
Hercules Chemical Corporation	New Rigid Rod Polymers	\$54,000	7/1/89 - 6/30/90
Solar Energy Research Institute	Wood Composites	\$27,000	7/1/89 - 6/30/90
Enichem	Thioether Polymers	\$13,000	7/1/89 - 6/30/90

## Part II

- A. Lon J. Mathias
- B. Ken Wynne/JoAnn Milliken
- C. 601-266-4871
- D. **New Thermal Curing Composite Matrices, Rigid Rod Polymers, and Solid-State NMR**

The synthetic portion of this project deals with 1,2-disubstituted cyclobutene monomers and oligomers plus the 1-cyclobutenecarboxylic amide derivatives of various diamenes and oligomers. Both systems are being examined with respect to self-addition and polymerization as well as reaction with added acetylene and maleimide-containing materials. Thermolysis of these materials is being used as the cure mechanism for composite matrices. Extension of the project into new areas has involved: solid-state NMR studies of nylons and aramids; implementation of a microcomputer-based NMR data station; and synthesis of two new families of rigid-rod polymers. Our primary work in solid-state  $^{15}\text{N}$  NMR analysis of nylons and nylon-containing materials has resulted in numerous publications and talks and is being extended to the evaluation of crystalline, amorphous, and interphase domains. Work on the NMR data station software is now complete and it will be offered to the polymer community for general use. Synthesis of the new rigid-rod systems has reached the point where excellent properties have been demonstrated in one family, and a key monomer has been synthesized in the other. The former involves thianthrenetetracarboxylic acid anhydride and imides therefrom. The latter is for a new family of A-B polyimide-benzoxazole materials.

### E. **Significant Results During the Last Year Include:**

- Successful synthesis and characterization of 1-cyclobutenecarboxylic acid derivatives and their initial characterizations.
- Complete characterization of nylon 6 and nylon 11 by various  $^{15}\text{N}$  NMR techniques.
- Synthesis of  $^{15}\text{N}$ -labeled nylon 12 and completion of polymer characterization in various crystal forms and analysis by solid-state NMR.
- Synthesis of several families of aramid model compounds, analysis of these materials by solution and solid-state NMR, and application of the data base thus generated to the evaluation of commercial aramids in solution and in the solid-state. The latter involves formation of various N-substituted derivatives with potential for random coil-rigid rod transformation.

- Synthesis of several members of the family of polyimides based on thianthrenetetracarboxylic acid.
- Synthesis of the key monomer intermediate, 4-hydroxy-5-nitrophthalimide.

**F. Plans for the Next Year's Work Include:**

- Completion of the NMR study of nylon 12.
- Synthesis of the  $^{15}\text{N}$ -labeled nylon 7 for evaluation by solid-state NMR in relation to piezoelectric properties and behavior.
- Synthesis of key monomers for obtaining fluorinated nylons with the goal of combining the molecular architecture of polyvinylidene fluoride with that of odd-numbered nylons such as nylon 7.
- Complete characterization of the thianthrene-containing polyimides.
- Scale-up of the synthesis of 4-hydroxy-5-aminophthalic derivatives for synthesis of A-B and AA-BB polyimide-benzoxazole materials.
- Final evaluation of the 1,2-disubstituted and 1-monosubstituted cyclobutene materials as thermocure systems for composites. This last will include thermoanalysis, DMA, and especially solid-state NMR.

**G. Graduate and Postdoctorals Currently Working on the Project Include:**

Paul K. Casey (full-time)

Ronald F. Colletti (full-time)

Douglas G. Powell (graduated 1989, part-time)

Rajendra Sundar (part-time, US citizen)

Randall A. Johnson (part-time beginning June 1, 1990)

William L. Jarrett (postdoctoral, full-time)



### Part III

#### Explanatory Text

Figure 1 is a view graph summarizing our results on nylon 12 solid-state NMR. Indicated are the  $^{13}\text{C}$  solid-state spectra of the amorphous and crystalline forms as indicated; the solid-state  $^{15}\text{N}$  CP/MAS spectra corresponding to the  $^{13}\text{C}$  spectra; and a table listing relaxation parameters for each component. The second view graph summarizes synthesis of the new family of thianthrene-containing polyimide precursor which we have recently obtained. These materials are readily converted to the polyimides which exhibit excellent thermoproperties with weight loss beginning in the TGA at above 550-600°C.

# NEW THERMAL CURING COMPOSITE MATRICES, RIGID ROD POLYMERS, AND SOLID STATE NMR

*Lon J. Mathias, Department of Polymer Science  
University of Southern Mississippi*

## SOLID STATE NMR OF DIFFERENT DOMAINS OF NYLON 12:

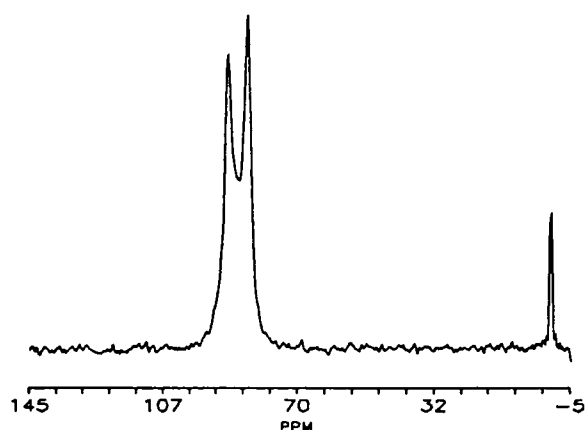


Figure 1.  $^{15}\text{N}$  solid state NMR spectrum of a mixture of  $\alpha$  and  $\gamma$  forms of nylon 12.

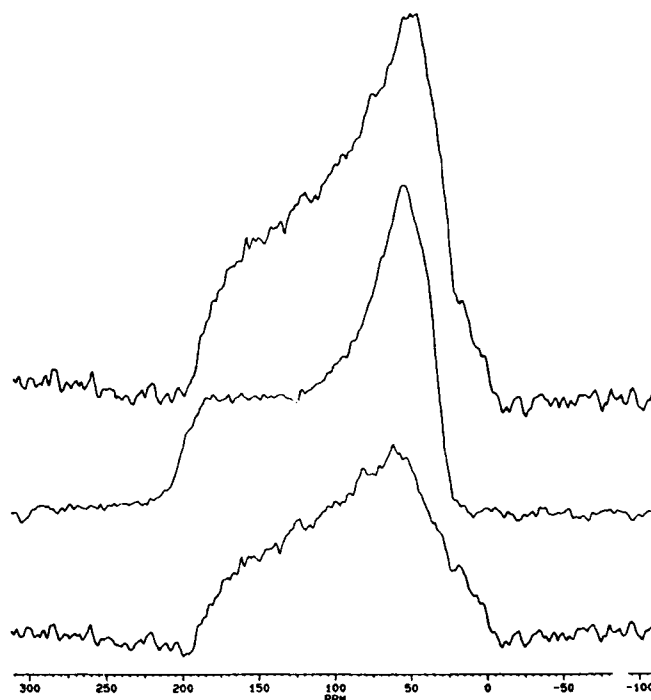


Figure 4.  $^{15}\text{N}$  chemical shift anisotropy (CSA) spectra for the mixture of  $\alpha$  plus  $\gamma$  (upper trace); melt-pressed  $\gamma$ -rich sample (middle); and spectral subtraction of middle from upper (lower).

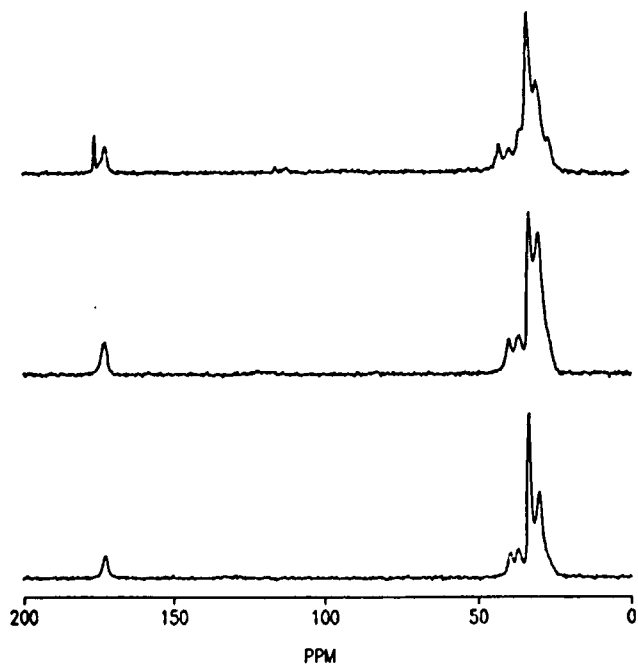


Figure 3.  $^{13}\text{C}$  solid state spectra of  $^{15}\text{N}$ -labelled nylon 12 in the annealed  $\gamma$  form (bottom trace); highly amorphous form (quenched, middle); and mixture of  $\alpha$  and  $\gamma$  form (upper).

Table.  $^{15}\text{N}$   $T_{1\rho}$  values (seconds) for nylon 12

CHEMICAL SHIFT (ppm)	90.3	89.3	87.0	84.2
quenched		108 / 3	131 / 4	
$\gamma$ (annealed)	319 / 11	314 / 20	41 / 4	
$\alpha + \gamma$		160 / 9	108 / 1	323 / 2

# NEW THERMAL CURING COMPOSITE MATRICES, RIGID ROD POLYMERS, AND SOLID STATE NMR

Lon J. Mathias, Department of Polymer Science  
University of Southern Mississippi

## NEW THIANTHRENE-CONTAINING RIGID ROD POLYIMIDES:

